PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 3/395, 3/36, 3/02, 3/39

A1

(11) Internati nal Publicati n Number: **WO 99/13040**

(43) Internati nal Publication Date: 18 March 1999 (18.03.99)

(21) International Application Number: PCT/IB98/01383

(22) International Filing Date: 7 September 1998 (07.09.98)

(30) Priority Data:
9719235.5 11 September 1997 (11.09.97) GB

(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: GUEDIRA, Nour–Eddine [MA/GB]; 115D Osborne Road, Jesmond, Newcastle upon Tyne NE2 2TA (GB). WARD, Dawn, Constance [GB/GB]; 3 Willerby Drive, Whitebridge Park, Gosforth, Newcastle upon Tyne NE3 5LL (GB).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

(81) Designated States: BR, CA, CN, CZ, HU, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DETERGENT COMPOSITIONS

(57) Abstract

The present invention relates to detergent compositions and in particular phosphate–containing detergent compositions and/or spray–dried particle–containing detergent compositions, which comprise a specific hydrophobic peroxyacid bleaching system, a heavy metal ion sequestrant system and an alkali earth metal salt. The compositions are particularly suitable for use in laundry washing methods.

BNSDOCID: <WO___9913040A1_I_>

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

BNSDOCID: <WO___9913040A1_I_>

Detergent Compositions

Technical Field

The present invention relates to detergent compositions and in particular phosphate-containing detergent compositions and /or spray-dried particle-containing detergent compositions, which comprise a specific hydrophobic peroxyacid bleaching system, a heavy metal ion sequestrant system and an alkali earth metal salt. The compositions are particularly suitable for use in laundry washing methods.

Background to the Invention

In the past decades research efforts have been directed towards the development of bleaching systems, based on organic peroxyacids, which can provide effective stain and/or soil removal from fabrics at lower wash temperatures. The organic peroxyacids are often obtained by the in situ perhydrolysis of organic peroxyacid bleach precursor compounds (bleach activators).

A commonly employed precursor compound is tetraacetyl ethylene diamine (TAED) which provides effective hydrophilic cleaning especially on beverage stains. Hydrophobic organic peroxyacid precursors have thus been developed to deal with hydrophobic stains and soils. Such hydrophobic organic peroxyacid precursors generally comprise long chain alkyl moieties carbon atoms. To achieve effective bleaching on hydrophobic and hydrophilic stains a bleach system comprising both hydrophobic and hydrophilic bleach precursors is preferably used. However, this increases the formulation costs and the formulation complexity.

A problem related to these bleach activators is that they have a tendency to catalytic decomposition in the wash and in particular at the fabric surface due to heavy metal

ions and high levels of metal ions present in the washing water and encrustation on the surface of the fabrics which will have accumulated during previous washes.

The problem is exacerbated by the tendency of these hydrophobic bleaches which generally comprise long chain alkyl moieties to migrate rapidly to the surface of fabrics under wash conditions.

Heavy metal ion sequestrants are commonly included in detergent compositions which comprise bleaching systems. The sequestrants act to sequester any heavy metal ions (e.g. Cu, Fe, Mn) in the laundry wash solution, or at the surface of the fabrics, which might otherwise give rise to wasteful catalytic decomposition of the peroxyacid species.

It is known that certain heavy metal ion sequestrants contain an amino linkage which is potentially oxidizable in a bleaching environment.

Thus, to ameliorate this problem of bleach-instability a second sequestrant which does not contain an oxidizable amino linkage can be employed in these bleach-containing detergent compositions.

However, it has now been found that in detergent compositions, even when comprising such a mixed sequestrant system, bleach systems still decompose due to the presence of heavy metal ions and/ or high levels of encrustation.

The inventors have found that this is a particular problem in detergent compositions containing high levels of phosphate-builder and/ or in detergent compositions containing spray-dried particles due to the higher levels of heavy metal ions present in these detergents. In particular, the process of formation of the spray-dried particle is performed by high temperatures and it has been found that thereby heavy metal ions, comprised in the reaction vessels/ spray-drying tower used in this process, can be introduced into the detergent composition.

The inventors now have found that the inclusion of a specific salt, in particular alkali earth metal salt, especially magnesium salt, can ameliorate the problem of bleach-instability of the sequestrants. It is believed that the salt forms a complex with the sequestrants, and in particular the amino-linkage of the sequestrant, whereby the

BNSDOCID: <WO 9913040A1 >

sequestrant becomes more stable and whereby even the chance of oxidisation of the sequestrant is reduced. This amounts to improved heavy metal ion and encrustation sequestering and thus and improved bleach performance.

The inventors have also found that these problems can be further ameliorated when a bleaching system is used which comprises a percarboxylic acid precursor or a percarboxylic acid, in particular those which have a shorter chain length than the hydrophobic bleach commonly employed. It is believed that this is due to this specific bleaching system having a reduced or delayed tendency to migrate to the fabric surface. It is believed that this allows sequestrants in the detergent composition to remove more heavy metal ions and metal ion encrustation from the fabric surface, before the hydrophobic bleach comes in contact with the metal ions. Furthermore, the delayed or reduced tendency of the hydrophobic bleach to migrate to the fabric surface is believed to reduce the chance of oxidation of the amino-linkage-containing sequestrants. In addition it has been found that this specific hydrophobic bleach has a good performance on both hydrophilic and hydrophobic stains, which thus reduces the need to formulate detergent compositions comprising a mixed bleach system.

The inventors have also found that when two types of sequestrants, a phosphonate-containing sequestrant and a carboxylate-containing sequestrant, are employed in these detergent compositions, the sequestering performance of the compositions in the wash is improved. It is believed that the phosphonate-containing sequestrant have their main sequestering performance on the fabric surface, while the carboxylate-containing sequestrant have their main sequestering performance in the wash solution. It is believed that this is the reason that an overall improved sequestering is achieved. This amounts to a reduced bleaching system decomposition and thus to an improved bleaching performance, and also to a reduced deposition of encrustation on the fabric and thus an improved softness of the fabrics.

Thus, the use in detergent compositions, in particular phosphate-builder comprising or spray-dried particle comprising compositions, of the specific salt has found to result in an improved stability of the sequestrants, leading to improved sequestering heavy metal ions. In addition, the use of the specific bleaching system amounts to an improved bleach stability of the sequestrants and improved bleach performance. Furthermore, the use of phosphonate-containing and carboxylate-containing

sequestrants results in an improved sequestering. This results in an overall improved bleaching performance, whiteness maintenance, and fabric softness. which can be even further improved by the use of the specific hydrophobic bleach.

All documents cited in the present description are, in relevant part, incorporated herein by reference.

Summary of the Invention

The present invention relates to a detergent composition comprising:

(a) from 0.1% to 80% by weight of the composition of a bleaching system comprising a percarboxylic acid precursor of formula:

$$R^1 - CO - L$$

wherein R^1 has at least 6 carbon atoms and L is a leaving group which is linked to the R^1 - CO- group with an oxygen atom.

(b) from 0.01% to 20% by weight of heavy metal ion sequestrants comprising at least one

(i) phosphonate-containing heavy metal ion sequestrants; and at least one

(ii) carboxylate-containing heavy metal ion sequestrants;

(c) from 0.1% to 10% by weight of an alkali earth metal salt.

The present invention also relates to a detergent composition comprising:

(a) from 0.1% to °0% by weight of the composition of a bleaching system comprising a percarboxylic acid of formula:

$$R^1\text{-}CO_3M$$

wherein R^1 has at least 6 carbon atoms, and M is a counterion;

(b) from 0.01% to 20% by weight of heavy metal ion sequestrants comprising at least one

(i) phosphonate-containing heavy metal ion sequestrants; and at least one

(ii) carboxylate-containing heavy metal ion sequestrants;

(c) from 0.1% to 10% by weight of an alkali earth metal salt.

Preferably, the detergent composition comprises phosphate-containing builder material and / or spray-dried particles.

Preferably, the detergent composition is a solid, preferably granular, detergent composition, preferably of bulk density of 330gr/litre to 600 gr/litre.

Detailed Description of the Invention

Bleaching System

An essential feature of detergent compositions of the invention is a bleaching system, present at a level of from 0.1% to 80% by, more preferably from 2% to 60% by weight, even more preferably from 5% to 40% by weight, most preferably from 7% to 30% by weight of the composition.

The bleaching system comprising a percarboxylic acid precursor of formula:

$$R^1 - CO - L$$

wherein n R^1 is essentially any functionality having at least 6 carbon atoms and L is a leaving group which is linked to the R^1 - CO- group with an oxygen atom.

Percarboxylic acid bleach precursor are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a percarboxylic acid.

On perhydrolysis the structure of the percarboxylic acid produced is:

$$R^1\text{-}CO_3M$$

wherein R^1 has at least 6 carbon atoms, and M is a counterion.

The counterion M preferably is sodium, potassium or hydrogen.

Alternatively, the detergent compositions of the invention comprises a bleaching system, comprising a peroxy acid of formula:

$$R^1\text{-}CO_3M$$

wherein R^1 has at least 6 carbon atoms, and M is a counterion.

The counterion M preferably is sodium, potassium or hydrogen.

Preferably the bleaching system comprises a source of hydrogen peroxide as described below. The provision of the percarboxylic acid occurs then by an in situ reaction of a (the) precursor with a source of hydrogen peroxide. However, in an alternative execution the bleaching system comprises a preformed peroxy acid, which is incorporated directly into the composition.

Compositions containing mixtures of a hydrogen peroxide source and a percarboxylic acid precursor in combination with a preformed peroxy acid are also envisaged.

The peroxy acid and the percarboxylic acid precursor of the invention preferably are 'hydrophobic' organic compounds whose parent carboxylic acid has a critical micelle

BNSDOCID: <WO 9913040A1 >

concentration less than 0.5 moles/litre and wherein said critical micelle concentration is measured in aqueous solution at 20°-50°C.

The percarboxylic acid formed from the precursor or the peroxy acid contains at least 7 carbon atoms, more preferably from 7 to 12 carbon atoms, more preferably from 8 to 11 carbon atoms, most preferably 9 carbon atoms (R_1 has thus from 6 to 12, preferably 7 to 10 and most preferably 8 carbon atoms). In a preferred aspect the percarboxylic acid formed from the precursor or the peroxy acid has an alkyl chain comprising at least 7 carbon atoms, more preferably at least 8 carbon atoms, most preferably 9 carbon atoms.

Percarboxylic Acid Precursor

The percarboxylic acid precursor can be any ester which had been described as a bleach activator for use in laundry detergents, for instance alkyl percarboxylic acid precursors described herein, sugar esters, such as pentaacetylglucose, esters of imidic acids such as ethyl benzimidate triacylcyanurates, such as triacetylcyanurate and tribenzoylcyanurate an esters giving relatively surface active oxidising products for instance of C_{8-18} -alkanoic or-aralkanoic acids such as described in GB-A-864798, GB-A-1147871 and the esters described in EP-A-98129 and EP-A-106634.

BNSDOCID: <WO___9913040A1_!_>

Alkyl Percarboxylic Acid Bleach Precursors

Alkyl percarboxylic acid bleach precursors are highly preferred precursors for the present invention.

Preferred can be phenyl esters of C_{14-22} - alkanoic or alkenoic acids, esters of hydroxylamine, geminal diesters of lower alkanoic acids and gem-idols, such as those described in EP-A-0125781 especially1,1,5-triacetoxypent-4-ene and 1,1,5,5-tetraacetoxypentane and the corresponding butene and butane compounds, ethylidene benzoate acetate and bis(ethylidene acetate) adipate and enol esters, for instance as described inEP-A-0140648 and EP-A-0092932.

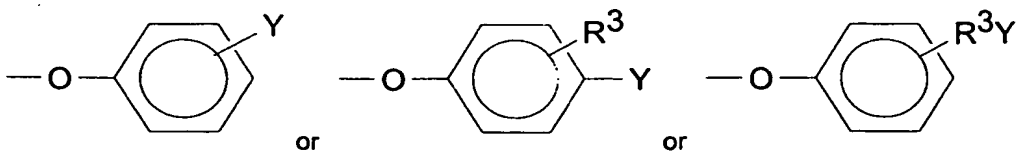
Other highly preferred alkyl percarboxylic acid precursors include decanoyloxy - benzenesulphonate sodium salt (DOBS) , benzoyloxy - benzenesulphonate sodium salt (BOBS), more preferred sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS) and even more preferred sodium nonanoyloxybenzene sulfonate (NOBS).

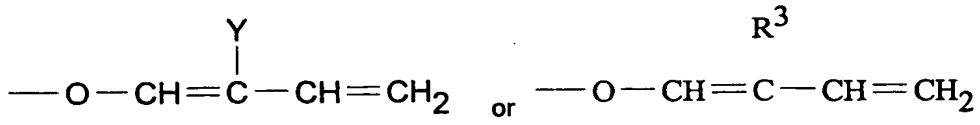
The percarboxylic acid precursor compounds present in the bleaching system are preferably incorporated at a level of from 0.05% to 20% by weight, more preferably from 0.1% to 15% by weight, most preferably from 0.2% to 10% by weight of the detergent compositions.

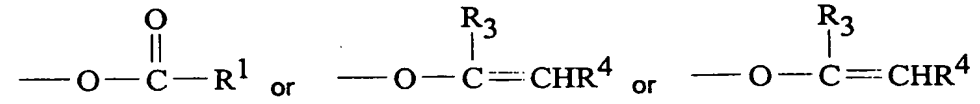
Leaving Groups

The percarboxylic acid precursor of the invention comprises a leaving group L. The leaving group L group must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:







and mixtures thereof, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3, and Y is H or a solubilizing group. Any of R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammmonium groups.

The preferred solubilizing groups are $-SO_3^-M^+$, $-CO_2^-M^+$, $-SO_4^-M^+$, $-N^+(R^3)_4X^-$ and O<--$N(R^3)_3$ and most preferably $-SO_3^-M^+$ and $-CO_2^-M^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

Preformed Organic Peroxy Acid

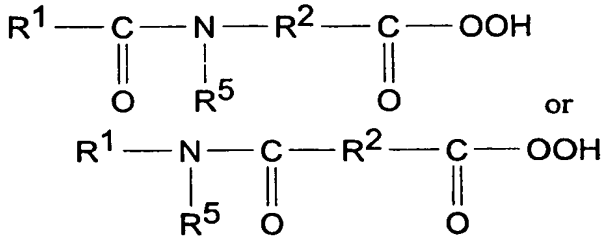
The bleaching system may contain as an alternative to the precursors mentioned above, or in addition to, a preformed peroxy acid, typically at a level of from 0.05% to 20% by weight, more preferably from 1% to 10% by weight of the detergent composition.

When the preformed peroxy acid is an alternative to the precursors mentioned above, and preferably when the preformed peroxy acid is present in addition to the precursors mentioned above, the peroxy acid has the general formula:

$$R^1\text{-}CO_3M$$

wherein R^1 has at least 6 carbon atoms, and M is a counterion.

A preferred class of peroxy acid compounds are the amide substituted compounds of the following general formulae:



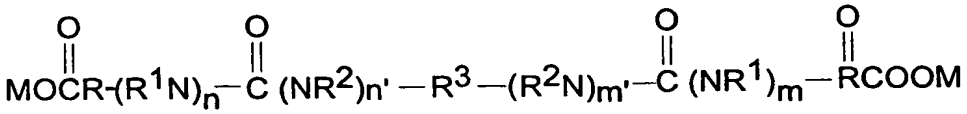
or

wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386. Suitable examples of this class of agents include (6-octylamino)-6-oxo-caproic acid, (6-nonylamino)-6-oxo-caproic acid, (6-decylamino)-6-oxo-caproic acid, magnesium monoperoxyphthalate hexahydrate, the salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 4,634,551, EP 0,133,354, U.S. 4,412,934 and EP 0,170,386.

A preferred preformed peroxyacid bleach compound for the purpose of the invention is mononononylamido peroxycarboxylic acid.

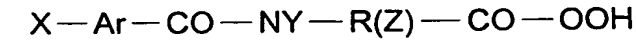
Other suitable organic peroxyacids include diperoxyalkanedioc acids having more than 7 carbon atoms, such as diperoxydodecanedioc acid (DPDA), diperoxytetradecanedioc acid and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid (PAP), nonanoylamido peroxo-adipic acid (NAPAA) and hexane sulphenoyl peroxypropionic acid and are also suitable herein.

Other suitable organic peroxyacids include diamino peroxyacids, which are disclosed in WO 95/ 03275, with the following general formula:



wherein:
R is selected from the group consisting of C_1-C_{12} alkylene, C_5-C_{12} cycloalkylene, C_6-C_{12} arylene and radical combinations thereof;
R^1 and R^2 are independently selected from the group consisting of H, C_1-C_{16} alkyl and C_6-C_{12} aryl radicals and a radical that can form a C_3-C_{12} ring together with R^3 and both nitrogens; R^3 is selected from the group consisting of C_1-C_{12} alkylene, C_5-C_{12} cycloalkylene and C_6-C_{12} arylene radicals; n and n' each are an integer chosen such that the sum thereof is 1; m and m' each are an integer chosen such that the sum thereof is 1; and
M is selected from the group consisting of H, alkali metal, alkaline earth metal, ammonium, alkanolammonium cations and radicals and combinations thereof.

Other suitable organic peroxyacids are include the amido peroxyacids which are disclosed in WO 95/ 16673, with the following general structure:



in which X represents hydrogen or a compatible substituent, Ar is an aryl group, R represents $(CH_2)_n$ in which n = 2 or 3, and Y and Z each represent independently a substituent selected from hydrogen or an alkyl or aryl or alkaryl group or an aryl group substituted by a compatible substituent provided that at least one of Y and Z is not hydrogen if n = 3. The substituent X on the benzene nucleus is preferably a

hydrogen or a meta or para substituent, selected from the group comprising halogen, typically chlorine atom, or some other non-released non-interfering species such as an alkyl group, conveniently up to C6 for example a methyl, ethyl or propyl group. Alternatively, X can represent a second amido-percarboxylic acid substituent of formula:-



in which R, Y, Z and n are as defined above.

Inorganic Perhydrate Bleaches

Inorganic perhydrate salts are a preferred source of hydrogen peroxide. These salts are normally incorporated in the form of the alkali metal, preferably sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product. Suitable coatings comprise inorganic salts such as alkali metal silicate, carbonate or borate salts or mixtures thereof, or organic materials such as waxes, oils, or fatty soaps.

Sodium perborate is a preferred perhydrate salt and can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates herein. Sodium percarbonate is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of use in the detergent compositions herein.

Heavy Metal Ion Sequestrant System

The detergent compositions of the invention contain as an essential component at least two heavy metal ion sequestrants. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

The total amount of heavy metal ion sequestrants present is of from 0.01% to 20%, preferably from 0.05% to 10%, more preferably from 0.2% to 7.5% and most preferably from 0.25% to 5% by weight of the detergent compositions.

The two heavy metal ion sequestrants of the invention are selected from phosphonate-containing heavy metal ion sequestrants and carboxylate- containing sequestrants. Preferably, these two types of sequestrants are present at a weight ratio of the former to the latter sequestrant of from 20:1 to 1:20, more preferably from 10:1 to 1:10 most preferably from 5:1 to 1:5.

Preferably, at least one of the sequestrants has no oxidisable amino linkage and/ or one of the sequestrants (preferably only one) has an oxidisable amino linkage and a carboxylate group. By oxidizable amino linkage it is particularly meant that the amino linkage can be oxidised under the oxidising/peroxidising conditions to be found in a laundry wash solution.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Phosphonate-Containing Heavy Metal Ion sequestrants

The phosphonate-containing heavy metal ion sequestrants, preferably those not having an oxidizable amino linkage, include any type of organo diphosphonates known in the art.

Suitable organo diphosphonates, which in addition provide crystal growth inhibition capacity, include the C_1-C_4 diphosphonates, more preferably the C_2 diphosphonates, such as ethylene diphosphonate, or most preferably ethane 1-hydroxy-1,1-diphosphonate (HEDP). The binding constant for HEDP at pH 10.4 is about 3.9 for Ca^{2+} ions, 4.3 for Mg^{2+} ions and 8.2 for copper ions.

Other suitable phosphonate-containing sequestrants include ethyclroric acids-derivatives.

Suitable phosphonate-containing heavy metal ion sequestrants having an oxidizable amino linkage include organic amino phosphonates, such as the amino alkylene poly (alkylene phosphonates). Preferred sequestrants of this type include ethylene diamine tetra methylene phosphonates and preferably diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) and hexamethylene diamine tetra (methylene phosphonate). Such phosphonates sequestrants are commercially available from Mansonto under the tradename Dequest®.

A preferred sequestrant can be amino tri (methylene phosphonic acid), in particularly in compositions for use as pre-treatment or soaking compositions.

Carboxylate-Containing Heavy Metal Ion Sequestrants

Suitable carboxylate-containing heavy metal ion sequestrants (having an amino linkage) include polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid (EDTA), ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid, diethylene triamine pentaacetate (DTPA)N- hydroxyethylethylenediamine triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanol-diglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine diacetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the tradename Trilon FS® and methyl glycine di-acetic acid (MGDA) or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β-alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N-N'-diglutaric acid (EDDG) and 2-hydroxypropylenediamine-N-N'-disuccinic acid (HPDDS) are also suitable.

Alkali Earth Salts

The detergent compositions of the invention comprise specific levels of alkali earth metal salts.

The salts are present at a level of from 0.1% to 10%, more preferably from 0.2% to 5%, most preferably from 0.2 to 3% by weight of the composition.

Preferably, the alkali earth salt is a calcium or magnesium salt.

The counterion is preferably carbonate, bicarbonate, chloride, bromide or fluoride, but most preferably sulphate.

The salts can be hydrated, but it can be preferred that anhydrous salts are used.

Additional Detergent Components

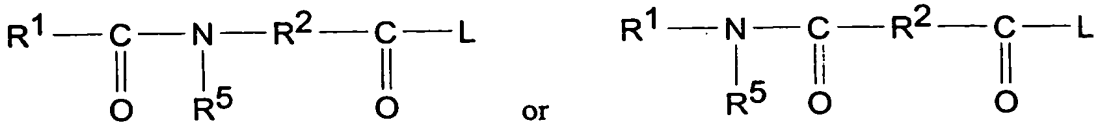
The detergent compositions or components thereof in accord with the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition or component, and the precise nature of the washing operation for which it is to be used.

The compositions or components thereof, of the invention preferably contain one or more additional detergent components selected from surfactants, additional bleaches, bleach catalysts, alkalinity systems, builders, phosphate-containing builders, organic polymeric compounds, enzymes, suds suppressors, lime soap, dispersants, soil suspension and anti-redeposition agents soil releasing agents, perfumes, brightners, photobleaching agents and additional corrosion inhibitors.

Additional Bleach System Components

Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N^1N^1 tetra acetylated alkylene diamines wherein the alkylene group contains at least 7 carbon atoms.

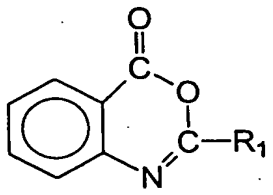
Preferred additional components of the bleaching system comprised in the detergent compositions of the invention peroxyacid precursors are amide substituted alkyl peroxyacid precursor compounds, including those of the following general formulae:



wherein R^1 is an aryl or alkaryl group with from about 1 to about 14 carbon atoms, R^2 is an alkylene, arylene, and alkarylene group containing from about 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from about 6 to 12 carbon atoms. R^2 preferably contains from about 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2. R^2 can include alkyl, aryl, wherein said R^2 may also contain halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Preferred examples of bleach precursors of this type include amide substituted peroxyacid precursor compounds selected from (6-octanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl) oxybenzene- sulfonate, and the highly preferred (6-nonanamidocaproyl)oxy benzene sulfonate, and mixtures thereof as described in EP-A-0170386.

Also suitable additional precursor compounds are of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:



wherein R_1 is an alkyl, alkaryl, aryl, or arylalkyl containing at least 5 carbon atoms.

Bleach Catalyst

The bleach system can contain a transition metal containing bleach catalyst.

One suitable type of bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

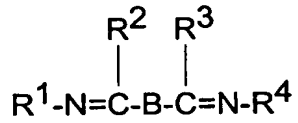
Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4$-$(ClO_4)_2$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)$(OCH_3)_3$-(PF_6).

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulsitol, mannitol, xylithol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

BNSDOCID: <WO 9913040A1 >

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with an non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R^1, R^2, R^3, and R^4 can each be selected from H, substituted alkyl and aryl groups such that each R^1-N=C-R^2 and R^3-C=N-R^4 form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S. CR^5R^6, NR^7 and C=O, wherein R^5, R^6, and R^7 can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe,-bispyridylmethane and -bispyridylamine complexes. Highly preferred catalysts include Co(2,2'-bispyridylamine)Cl_2, Di(isothiocyanato)bispyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, Co(2,2-bispyridylamine)$_2O_2ClO_4$, Bis-(2,2'-bispyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including $N_4Mn^{III}(u\text{-}O)_2Mn^{IV}N_4)^+$and [$Bipy_2Mn^{III}(u\text{-}O)_2Mn^{IV}bipy_2$]-$(ClO_4)_3$.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with

manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

The bleach catalyst is typically used in a catalytically effective amount in the compositions and processes herein. By "catalytically effective amount" is meant an amount which is sufficient, under whatever comparative test conditions are employed, to enhance bleaching and removal of the stain or stains of interest from the target substrate. The test conditions will vary, depending on the type of washing appliance used and the habits of the user. Some users elect to use very hot water; others use warm or even cold water in laundering operations. Of course, the catalytic performance of the bleach catalyst will be affected by such considerations, and the levels of bleach catalyst used in fully-formulated detergent and bleach compositions can be appropriately adjusted. As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 1 ppm to about 200 ppm of the catalyst species in the wash liquor. To illustrate this point further, on the order of 3 micromolar manganese catalyst is effective at 40°C, pH 10 under European conditions using perborate and a bleach precursor. An increase in concentration of 3-5 fold may be required under U.S. conditions to achieve the same results.

Surfactant

The detergent compositions or components thereof in accord with the invention preferably contain one or more surfactants selected from anionic, nonionic, cationic, ampholytic, amphoteric and zwitterionic surfactants and mixtures thereof.

A typical listing of anionic, nonionic, ampholytic, and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December 30, 1975. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981.

Where present, ampholytic, amphoteric and zwitteronic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

BNSDOCID: <WO 9913040A1 >

Anionic Surfactant

The detergent compositions or compositions thereof in accord with the present invention preferably comprise an additional anionic surfactant. Essentially any anionic surfactants useful for detersive purposes can be comprised in the detergent composition. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic Sulfate Surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C_{10}-C_{18} alkyl sulfates, more preferably the C_{11}-C_{15} branched chain alkyl sulfates and the C_{12}-C_{14} linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_{10}-C_{18} alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_{11}-C_{18}, most preferably C_{11}-C_{15} alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic Sulfonate Surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

BNSDOCID: <WO 9813040A1 >

Anionic Carboxylate Surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_20)_x$ $CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali Metal Sarcosinate Surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Alkoxylated Nonionic Surfactant

Essentially any alkoxylated nonionic surfactants are suitable herein. The ethoxylated and propoxylated nonionic surfactants are preferred.

Preferred alkoxylated surfactants can be selected from the classes of the nonionic condensates of alkyl phenols, nonionic ethoxylated alcohols, nonionic ethoxylated/propoxylated fatty alcohols, nonionic ethoxylate/propoxylate condensates with propylene glycol, and the nonionic ethoxylate condensation products with propylene oxide/ethylene diamine adducts.

Nonionic Alkoxylated Alcohol Surfactant

The condensation products of aliphatic alcohols with from 1 to 25 moles of alkylene oxide, particularly ethylene oxide and/or propylene oxide, are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

Nonionic Polyhydroxy Fatty Acid Amide Surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, ethoxy, propoxy, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic Fatty Acid Amide Surfactant

Suitable fatty acid amide surfactants include those having the formula: $R^6CON(R^7)_2$ wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

BNSDOCID: <WO 9913040A1 >

Nonionic Alkylpolysaccharide Surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from 6 to 30 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from 1.3 to 10 saccharide units.

Preferred alkylpolyglycosides have the formula:

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18 carbon atoms; n is 2 or 3; t is from 0 to 10, and x is from 1.3 to 8. The glycosyl is preferably derived from glucose.

Amphoteric Surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^0(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions or components thereof in accord with the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, each R^1 is typically C_1-C_3 alkyl, and R^2 is a C_1-C_5 hydrocarbyl group. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Cationic Surfactants

Suitable cationic surfactants to be used in the detergent compositions or components thereof herein include the quaternary ammonium surfactants. Preferably the quaternary ammonium surfactant is a mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or

alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups. Preferred are also the mono-alkoxylated and bis-alkoxylated amine surfactants.

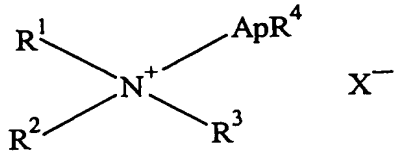
Another suitable group of cationic surfactants which can be used in the detergent compositions or components thereof herein are cationic ester surfactants. The cationic ester surfactant is a, preferably water dispersible, compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group.

Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

In one preferred aspect the ester linkage and cationically charged group are separated from each other in the surfactant molecule by a spacer group consisting of a chain comprising at least three atoms (i.e. of three atoms chain length), preferably from three to eight atoms, more preferably from three to five atoms, most preferably three atoms. The atoms forming the spacer group chain are selected from the group consisting of carbon, nitrogen and oxygen atoms and any mixtures thereof, with the proviso that any nitrogen or oxygen atom in said chain connects only with carbon atoms in the chain. Thus spacer groups having, for example, -O-O- (i.e. peroxide), -N-N-, and -N-O- linkages are excluded, whilst spacer groups having, for example -CH_2-O- CH_2- and -CH_2-NH-CH_2- linkages are included. In a preferred aspect the spacer group chain comprises only carbon atoms, most preferably the chain is a hydrocarbyl chain.

Cationic mono-alkoxylated amine surfactants

The cationic mono-alkoxylated amine surfactant are preferably of the general formula I:

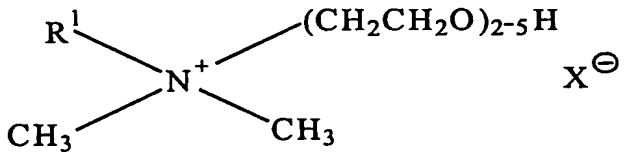


(I)

wherein R^1 is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 14 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl, most preferably both R^2 and R^3 are methyl groups; R^4 is selected from hydrogen (preferred), methyl and ethyl; X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is a alkoxy group, especially a ethoxy, propoxy or butoxy group; and p is from 0 to about 30, preferably 2 to about 15, most preferably 2 to about 8, with the proviso that if A is ethoxy and R_4 is hydrogen and p is 1, R_1 is not a C_{12}-C_{14} alkyl group.

Preferably the ApR^4 group in formula I has p=1 and is a hydroxyalkyl group, having no greater than 6 carbon atoms whereby the —OH group is separated from the quaternary ammonium nitrogen atom by no more than 3 carbon atoms. Particularly preferred ApR^4 groups are —CH_2CH_2OH, —$CH_2CH_2CH_2OH$, —$CH_2CH(CH_3)OH$ and —$CH(CH_3)CH_2OH$, with —CH_2CH_2OH being particularly preferred. Preferred R^1 groups have have no greater than 10 carbon atoms, or even no greater than 8 or 9 carbon atoms. Preferred R^1 groups are linear alkyl groups. Linear R^1 groups having from 8 to 11 carbon atoms, or from 8 to 10 carbon atoms are preferred. Such a cationic surfactant which is highly preferred has a formula wherein R_1 is a C_8-C_{10} alkyl group, p is 1, A is ethoxy and R_2 and R_3 are methyl groups.

Another highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



wherein R^1 is C_{10}-C_{18} hydrocarbyl and mixtures thereof, especially C_{10}-C_{14} alkyl, preferably C_{10} and C_{12} alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

As noted, compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy, isopropoxy [$CH(CH_3)CH_2O$] and

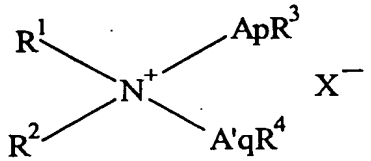
BNSDOCID: <WO 9913040A1 >

[$CH_2CH(CH_3O]$ units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The levels of the cationic mono-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

Cationic bis-alkoxylated amine surfactant

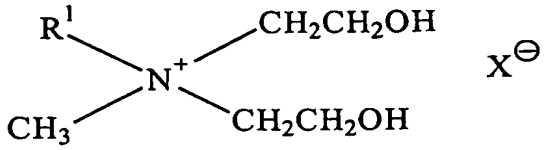
The cationic bis-alkoxylated amine surfactant preferably has the general formula II:



(II)

wherein R^1 is an alkyl or alkenyl moiety containing from about 8 to about 18 carbon atoms, preferably 10 to about 16 carbon atoms, most preferably from about 10 to about 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C_1-C_4 alkoxy, especially ethoxy, (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

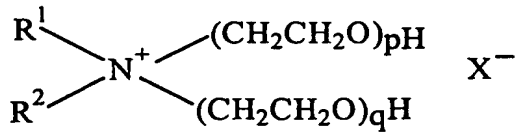
Highly preferred cationic bis-alkoxylated amine surfactants for use herein are of the formula



wherein R^1 is C_{10}-C_{18} hydrocarbyl and mixtures thereof, preferably C_{10}, C_{12}, C_{14} alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxylated amine structure noted above, since in a preferred compound R^1 is derived from (coconut)

C_{12}-C_{14} alkyl fraction fatty acids, R^2 is methyl and ApR^3 and $A'qR^4$ are each monoethoxy.

Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R^1 is C_{10}-C_{18} hydrocarbyl, preferably C_{10}-C_{14} alkyl, independently p is 1 to about 3 and q is 1 to about 3, R^2 is C_1-C_3 alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy (Bu) isopropoxy [$CH(CH_3)CH_2O$] and [$CH_2CH(CH_3O$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The levels of the cationic bis-alkoxylated amine surfactants used in detergent compositions of the invention is preferably from 0.1% to 20%, more preferably from 0.4% to 7%, most preferably from 0.5% to 3.0% by weight of the composition.

Water-Soluble Builder Compound

The detergent compositions or components thereof in accord with the present invention preferably contain a water-soluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition.

The detergent compositions of the invention preferably comprise phosphate-containing builder material. Preferably present at a level of from 0.015 to 50%, more preferably from 5% to 30%, more preferably from 8% to 25%, most preferably from 12% to 205 by weight of the composition.

The phosphate-containing builder material preferably comprises tetrasodium pyrophosphate or even more preferably anhydrous sodium tripolyphosphate.

BNSDOCID: <WO___9913040A1 I >

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, borates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates or their acids containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447. The most preferred polycarboxylic acid containing three carboxy groups is citric acid, preferably present a t a level of from 0.1% to 15%, more preferably from 0.5% to 8% by weight of the composition.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially Soluble or Insoluble Builder Compound

The detergent compositions or compositions thereof in accord with the present invention may contain a partially soluble or insoluble builder compound, typically present in detergent compositions at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition.

Examples of largely water insoluble builders include the sodium aluminosilicates.

Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. xH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula:

$$Na_{12}[AlO_2)_{12}(SiO_2)_{12}].\ xH_2O$$

wherein x is from 20 to 30, especially 27. Zeolite X has the formula Na_{86} $[(AlO_2)_{86}(SiO_2)_{106}].\ 276\ H_2O$.

Another preferred aluminosilicate zeolite is zeolite MAP builder. The zeolite MAP can be present at a level of from 1% to 80%, more preferably from 15% to 40% by weight of the compositions.

Zeolite MAP is described in EP 384070A (Unilever). It is defined as an alkali metal alumino-silicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, preferably within the range from 0.9 to 1.33 and more preferably within the range of from 0.9 to 1.2.

Of particular interest is zeolite MAP having a silicon to aluminium ratio not greater than 1.15 and, more particularly, not greater than 1.07.

In a preferred aspect the zeolite MAP detergent builder has a particle size, expressed as a d_{50} value of from 1.0 to 10.0 micrometres, more preferably from 2.0 to 7.0 micrometres, most preferably from 2.5 to 5.0 micrometres.

The d_{50} value indicates that 50% by weight of the particles have a diameter smaller than that figure. The particle size may, in particular be determined by conventional analytical techniques such as microscopic determination using a scanning electron microscope or by means of a laser granulometer. Other methods of establishing d_{50} values are disclosed in EP 384070A.

Enzyme

Another preferred ingredient useful in the detergent compositions or components thereof is one or more additional enzymes.

Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, cellulases, endolases, esterases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem

by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α-amylases obtained from a special strain of B licheniformis, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp., Thermomyces sp. or Pseudomonas sp. including Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Organic Polymeric Compound

Organic polymeric compounds are preferred additional components of the detergent compositions or components thereofin accord with the invention, and are preferably present as components of any particulate components where they may act such as to bind the particulate component together. By organic polymeric compound it is meant herein essentially any polymeric organic compound commonly used as dispersants,

and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein, not being an quaternised ethoxylated (poly) amine clay-soil removal/ anti-redeposition agent in accord with the invention.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

Suds Suppressing System

The detergent compositions of the invention, when formulated for use in machine washing compositions, preferably comprise a suds suppressing system present at a

level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds and 2-alkyl alcanol antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types. Preferred silicone antifoam compounds are the siloxanes, particularly the polydimethylsiloxanes having trimethylsilyl end blocking units.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

A preferred suds suppressing system comprises:

(a) antifoam compound, preferably silicone antifoam compound, most preferably a silicone antifoam compound comprising in combination

(i) polydimethyl siloxane, at a level of from 50% to 99%, preferably 75% to 95% by weight of the silicone antifoam compound; and

(ii) silica, at a level of from 1% to 50%, preferably 5% to 25% by weight of the silicone/silica antifoam compound;

wherein said silica/silicone antifoam compound is incorporated at a level of from 5% to 50%, preferably 10% to 40% by weight;

(b) a dispersant compound, most preferably comprising a silicone glycol rake copolymer with a polyoxyalkylene content of 72-78% and an ethylene oxide to propylene oxide ratio of from 1:0.9 to 1:1.1, at a level of from 0.5% to 10%, preferably 1% to 10% by weight; a particularly preferred silicone glycol rake copolymer of this type is DCO544, commercially available from DOW Corning under the tradename DCO544;

(c) an inert carrier fluid compound, most preferably comprising a C_{16}-C_{18} ethoxylated alcohol with a degree of ethoxylation of from 5 to 50, preferably 8 to 15, at a level of from 5% to 80%, preferably 10% to 70%, by weight;

A highly preferred particulate suds suppressing system is described in EP-A-0210731 and comprises a silicone antifoam compound and an organic carrier material having a melting point in the range 50°C to 85°C, wherein the organic carrier material comprises a monoester of glycerol and a fatty acid having a carbon chain containing from 12 to 20 carbon atoms. EP-A-0210721 discloses other preferred particulate suds suppressing systems wherein the organic carrier material is a fatty acid or alcohol having a carbon chain containing from 12 to 20 carbon atoms, or a mixture thereof, with a melting point of from 45°C to 80°C.

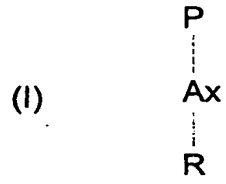
Polymeric Dye Transfer Inhibiting Agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

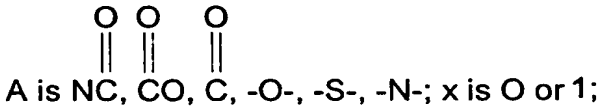
The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof, whereby these polymers can be cross-linked polymers.

a) Polyamine N-Oxide Polymers

Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :

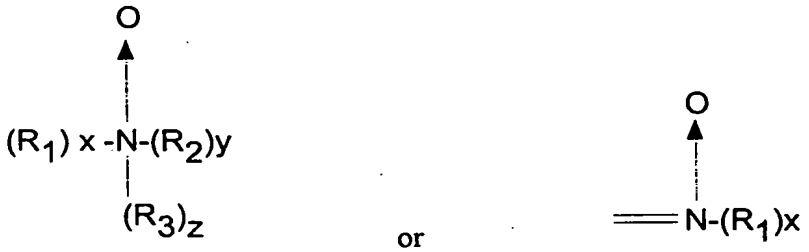


wherein P is a polymerisable unit, and



R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



BNSDOCID: <WO 9913040A1 >

wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general formula (I) wherein R is an aromatic,heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

<u>b) Copolymers of N-Vinylpyrrolidone and N-Vinylimidazole</u>

Suitable herein are coploymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

<u>c) Polyvinylpyrrolidone</u>

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

BNSDOCID: <WO 9913040A1 >

d) Polyvinyloxazolidone

The detergent compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000.

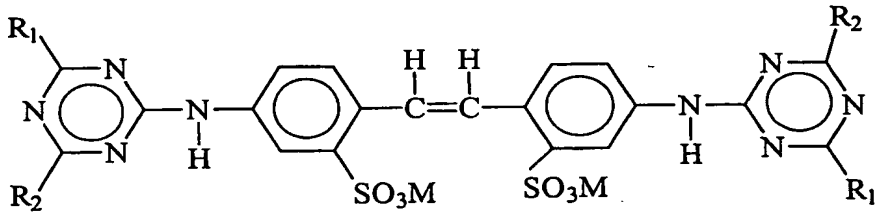
e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical Brightener

The detergent compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Polymeric Soil Release Agent

Known polymeric soil release agents, hereinafter "SRA", can optionally be employed in the present detergent compositions. If utilized, SRA's will generally comprise from 0.01% to 10.0%, typically from 0.1% to 5%, preferably from 0.2% to 3.0% by weight, of the compositions.

Preferred SRA's typically have hydrophilic segments to hydrophilize the surface of hydrophobic fibers such as polyester and nylon, and hydrophobic segments to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles, thereby serving as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the SRA to be more easily cleaned in later washing procedures.

Preferred SRA's include oligomeric terephthalate esters, typically prepared by processes involving at least one transesterification/oligomerization, often with a metal catalyst such as a titanium(IV) alkoxide. Such esters may be made using additional monomers capable of being incorporated into the ester structure through one, two, three, four or more positions, without, of course, forming a densely crosslinked overall structure.

Suitable SRA's include a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and allyl-derived sulfonated terminal moieties covalently attached to the

BNSDOCID: <WO 9913040A1 >

backbone, for example as described in U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Such ester oligomers can be prepared by: (a) ethoxylating allyl alcohol; (b) reacting the product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol ("PG") in a two-stage transesterification/oligomerization procedure; and (c) reacting the product of (b) with sodium metabisulfite in water. Other SRA's include the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al., for example those produced by transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"). Other examples of SRA's include: the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, methyl (Me)-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al., the latter being typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT, optionally but preferably further comprising added PEG, e.g., PEG 3400.

SRA's also include: simple copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, see U.S. 3,959,230 to Hays, May 25, 1976 and U.S. 3,893,929 to Basadur, July 8, 1975; cellulosic derivatives such as the hydroxyether cellulosic polymers available as METHOCEL from Dow; the C_1-C_4 alkyl celluloses and C_4 hydroxyalkyl celluloses, see U.S. 4,000,093, December 28, 1976 to Nicol, et al.; and the methyl cellulose ethers having an average degree of substitution (methyl) per anhydroglucose unit from about 1.6 to about 2.3 and a solution viscosity of from about 80 to about 120 centipoise measured at 20°C as a 2% aqueous solution. Such materials are available as METOLOSE SM100 and METOLOSE SM200, which are the trade names of methyl cellulose ethers manufactured by Shin-etsu Kagaku Kogyo KK.

Additional classes of SRA's include: (I) nonionic terephthalates using diisocyanate coupling agents to link polymeric ester structures, see U.S. 4,201,824, Violland et al. and U.S. 4,240,918 Lagasse et al.; and (II) SRA's with carboxylate terminal groups made by adding trimellitic anhydride to known SRA's to convert terminal hydroxyl groups to trimellitate esters. With the proper selection of catalyst, the trimellitic anhydride forms linkages to the terminals of the polymer through an ester of the isolated carboxylic acid of trimellitic anhydride rather than by opening of the anhydride linkage. Either nonionic or anionic SRA's may be used as starting materials as long as they have hydroxyl terminal groups which may be esterified. See U.S. 4,525,524 Tung et al.. Other classes include: (III) anionic terephthalate-based SRA's of the urethane-linked variety, see U.S. 4,201,824, Violland et al.;

Other Optional Ingredients

Other optional ingredients suitable for inclusion in the compositions of the invention include perfumes, colours and filler salts, with sodium sulfate being a preferred filler salt.

Highly preferred compositions contain from about 2% to about 10% by weight of an organic acid, preferably citric acid. Also, preferably combined with a carbonate salt, minor amounts (e.g., less than about 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides and dyes, such as those described in US Patent 4,285,841 to Barrat et al., issued August 25, 1981 (herein incorporated by reference), can be present.

Form of the Compositions

The detergent component of the invention can be made via a variety of methods, including dry-mixing and agglomerating of the various compounds comprised in the detergent component.

The detergent component preferably forms part of a detergent composition. The compositions in accordance with the invention can take a variety of physical forms including liquid and solid forms such as tablet, flake, pastille and bar, and preferably granular forms.

The compositions in accord with the present invention can also be used in or in combination with bleach additive compositions, for example comprising chlorine bleach.

Chlorine-Based Bleach

The detergent compositions can include as an additional component a chlorine-based bleach. However, since preferred detergent compositions of the invention are solid, most liquid chlorine-based bleaching will not be suitable for these detergent compositions and only granular or powder chlorine-based bleaches will be suitable.

Alternatively, the detergent compositions can be formulated such that they are chlorine-based bleach-compatible, thus ensuring that a chlorine based bleach can be added to the detergent composition by the user at the beginning or during the washing process.

The chlorine-based bleachis such that a hypochlorite species is formed in aqueous solution. The hypochlorite ion is chemically represented by the formula OCl^-.

Those bleaching agents which yield a hypochlorite species in aqueous solution include alkali metal and alkaline earth metal hypochlorites, hyposchlorite addition products, chloramines, chlorimines, chloramides, and chlorimides. Specific examples of compounds of this type include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, sodium dichloroisocyanurate sodium dichloroisocyanurate dihydrate, trichlorocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, chloramine B and Dichloramine B. A preferred bleaching agent for use in the compositions of the instant invention is sodium hypochlorite, potassium hypochlorite, or a mixture thereof.. A preferred chlorine-based bleach can be Triclosan (trade name).

Most of the above-described hypochlorite-yielding bleaching agents are available in solid or concentrated form and are dissolved in water during preparation of the compositions of the instant invention. Some of the above materials are available as aqueous solutions.

In general, granular detergent compositions in accordance with the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation. The quaternised clay-soil removal/ anti-redeposition agent in accord with the present invention can be added to the other detergent components by dry-mixing, agglomeration (preferably combined with a carrier material) or as a spray-dried component.

The mean particle size of the components of granular compositions in accordance with the invention, should preferably be such that no more that 25% of the particles are greater than 1.8mm in diameter and not more than 25% of the particles are less than 0.25mm in diameter. Preferably the mean particle size is such that from 10% to 50% of the particles has a particle size of from 0.2mm to 0.7mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of sieves, preferably Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

The bulk density of granular detergent compositions in accordance with the present invention typically have a bulk density of at least 200 g/litre, more preferably from 300 g/litre to 1200 g/litre, more preferably from 300g/litre to 800 gr/litre, most preferably from 330 g/litre to 600 gr/ lite. Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm high and has internal diameters of 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement eg; a knife, across its upper edge. The filled cup is then

weighed and the value obtained for the weight of powder doubled to provide a bulk density in g/litre. Replicate measurements are made as required.

Laundry Washing Method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is meant from 10g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect the detergent composition is formulated such that it is suitable for hand washing.

In another preferred aspect the detergent composition is a pre-treatment or soaking composition, to be used to pre-treat or soak soiled and stained fabrics.

Abbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

	LAS	:	Sodium linear C_{11-13} alkyl benzene sulfonate
	TAS	:	Sodium tallow alkyl sulfate
	CxyAS	:	Sodium C_{1x} - C_{1y} alkyl sulfate
	C46SAS	:	Sodium C_{14} - C_{16} secondary (2,3) alkyl sulfate
	CxyEzS	:	Sodium C_{1x}-C_{1y} alkyl sulfate condensed with z moles of ethylene oxide
	CxyEz	:	C_{1x}-C_{1y} predominantly linear primary alcoholcondensed with an average of z moles of ethylene oxide
	QAS	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$ - C_{14}
	QAS 1	:	$R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_8$ - C_{11}
	APA	:	C_8 - C_{10} amido propyl dimethyl amine
	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
	STS	:	Sodium toluene sulphonate
	CFAA	:	C_{12}-C_{14} (coco) alkyl N-methyl glucamide
	TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide
	TPKFA	:	C_{12}-C_{14} topped whole cut fatty acids
	STPP	:	Anhydrous sodium tripolyphosphate
	TSPP	:	Tetrasodium pyrophosphate
	Zeolite A	:	Hydrated sodium aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12}.27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
	NaSKS-6	:	Crystalline layered silicate of formula δ- $Na_2Si_2O_5$
	Citric acid	:	Anhydrous citric acid
	Borate	:	Sodium borate
	Carbonate	:	Anydrous sodium carbonate with a particle size between 200μm and 900μm
	Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400μm and 1200μm
	Silicate	:	Amorphous sodium silicate (SiO_2:Na_2O = 2.0:1)

Sulfate	:	Anhydrous sodium sulfate
Mg sulfate	:	Anhydrous magnesium sulfate
Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
ATC	:	Acetyl triethyl citrate
MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA (1)	:	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
AA	:	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	:	Sodium carboxymethyl cellulose
Cellulose ether	:	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
Protease	:	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
Protease I	:	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	:	Proteolytic enzyme, having 5.3% by weight of ctive enzyme, sold by NOVO Industries A/S
Cellulase	:	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
Amylase	:	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
Lipase	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
Lipase (1)	:	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
Endolase	:	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S

PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_2.3H_2O.H_2O_2$
PB1	:	Anhydrous sodium perborate bleach of nominal formula $NaBO_2.H_2O_2$
Percarbonate	:	Sodium percarbonate of nominal formula $2Na_2CO_3.3H_2O_2$
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt
DOBS	:	Decanoyl oxybenzene sulphonate in the form of the sodium salt
DPDA	:	Diperoxy dodecanedioc acid
TAED	:	Tetraacetylethylenediamine
DTPA	:	Diethylene triamine pentaacetic acid
DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
HEDP	:	1,1-hydroxyethane diphosphonic acid
EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
ATMP	:	amino tri (methylene phosphonic acid)
EDDG	:	Ethylenediamine-N,N' diglutaric acid
Photoactivated	:	Sulfonated zinc phthlocyanine encapsulated in bleach (1) dextrin soluble polymer
Photoactivated	:	Sulfonated alumino phthlocyanine encapsulated in bleach (2) dextrin soluble polymer
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate
PEGx	:	Polyethylene glycol, with a molecular weight of x (typically 4,000)
PEO	:	Polyethylene oxide, with an average molecular weight of 50,000
TEPAE	:	Tetraethylenepentaamine ethoxylate
PVI	:	Polyvinyl imidosole, with an average molecular weight of 20,000
PVP	:	Polyvinylpyrolidone polymer, with an average molecular weight of 60,000

BNSDOCID: <WO 9913040A1 I >

PVNO	:	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
PVPVI	:	Copolymer of polyvinylpyrolidone and vinylimidazole, with an average molecular weight of 20,000
QEA	:	bis($(C_2H_5O)(C_2H_4O)_n$)(CH_3) -N^+-C_6H_{12}-N^+-(CH_3) bis((C_2H_5O)-(C_2H_4O))$_n$, wherein n = from 20 to 30
SRP 1	:	Anionically end capped poly esters
SRP 2	:	Diethoxylated poly (1, 2 propylene terephtalate) short block polymer
PEI	:	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogel
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
Opacifier	:	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
Wax	:	Paraffin wax

In the following examples all levels are quoted as % by weight of the composition:

Example 1

The following detergent formulations were prepared in accord with the invention.

	A	B	C	D
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	-	0.4	0.2	0.4
HEDP	0.7	-	0.2	-
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
ATMP	-	-	-	0.5
HEDP	-	1.0	0.2	0.2
EDDS	0.3	0.9	0.5	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-

BNSDOCID: <WO___9913040A1_I_>

PB4	-	18.0	-	21.5
PB_1	-	-	15.0	-
NOBS	3.0	2.0	4.0	6.0
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
$MgSO_4$	0.7	1.1	2.0	1.7
Misc/minor to 100%				

Example 2

The following granular detergent formulations were prepared in accord with the invention.

	E	F	G	H	I	J
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA (1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
EDDS	1.0	0.3	-	0.2	0.4	0.5
HEDP	0.5	-	-	0.5	-	-
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0

Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	2.0
DPDA	-	-	-	-	3.0	-
DOBS	-	2.0	-	5.0	-	-
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	1.0	1.0	0.2	0.4	0.2	0.5
ATMP	0.5	-	-	-	-	-
HEDP	-	0.4	0.2	-	0.6	0.2
EDDG	-	-	0.2	0.2	-	-
Misc/minors to 100%						

Example 3

The following granular detergent formulations were prepared in accord with the invention.

	K	L	M	N
Base granule				
STPP	-	3.0	-	1.8
Zeolite A	30.0	-	24.0	-
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	0.2	0.4	0.7	-
EDDS	0.4	-	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1
Cellulase	0.1	0.2	0.2	0.1

BNSDOCID: <WO___9913040A1_I_>

NOBS	-	4.0	-	4.5
PB1	-	5.0	1.5	6.0
DOBS	4.0	-	8.0	0.5
PB4	7.0	-	5.0	-
$MgSO_4$	0.5	0.9	0.2	2.0
EDDS	-	0.2	-	0.7
HEDP	0.2	-	0.4	0.4
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-
Sud supressor	-	0.5	0.5	-
Misc/minor to 100%				

BNSDOCID: <WO___9913040A1_I_>

Example 4

The following granular detergent compositions were prepared in accord with the invention.

	O	P	Q
Blown powder			
Zeolite A	20.0	-	-
STPP	-	20.0	15.0
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	-
DTPA	-	-	0.4
STS	-	-	1.0
Spray on			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
$MgSO_4$	3.0	1.0	0.8
PB1	1.5	2.0	-
PB4	18.5	13.0	-
NOBS	2.0	7.0	-
DOBS	-	-	3.0
Percarbonate	-	-	15.0
QAS (I)	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15ppm

BNSDOCID: <WO___9913040A1_I_>

HEDP	2.0	-	0.1
EDDS	0.3	0.9	0.3
SKS-6	-	-	3.0
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
Misc/minors to 100%			

Example 5

The following detergent compositions, according to the present invention were prepared:

	R	S	T
Blown Powder			
STPP	15.0	15.0	-
Zeolite A	-	-	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	-
EDDS	0.3	1.0	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
HEDP	-	0.2	0.1
DTPA	0.2	-	0.4
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
NOBS	6.0	2.0	-
Dry Additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
DOBS	-	-	5.0
PB1	14.0	7.0	-

BNSDOCID: <WO 9913040A1 I >

$MgSO_4$	0.3	2.6	1.5
PB_4	-	7.0	10.0
PEO	-	-	0.2
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 6

The following detergent formulations, containing a spray-dried component, according to the present invention were prepared:

	U	V	W	X	Y	Z
LAS	18.0	14.0	24.0	20.0	12.0	16.0
QAS	0.7	1.0	-	0.7	-	0.5
TFAA	-	1.0	-	-	-	1.0
C23E56.5	-	-	1.0	-	-	-
C45E7	-	1.0	-	-	-	-
C45E3S	1.0	2.5	1.0	-	2.0	3.0
STPP	32.0	18.0	30.0	22.0	25.0	14.0
Silicate	9.0	5.0	9.0	8.0	5.0	7.0
Carbonate	11.0	7.5	10.0	5.0	12.0	7.0
Bicarbonate	-	7.5	-	-	-	2.0
PB1	3.0	1.0	7.0	-	-	-
PB4	-	1.0	-	-	-	-
Percarbonate	-	-	-	-	2.0	5.0
NOBS	2.0	1.0	-	-	-	3.0
DOBS	-	1.0	6.0	-	2.0	-
DTPMP	-	1.0	-	-	-	1.0
DTPA	0.5	-	0.2	0.3	-	-
EDDS	0.5	0.2	-	0.5	0.7	-
HEDP	-	0.2	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1	0.1	0.4
MA/AA	1.0	1.5	2.0	0.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2	0.4	0.6
PEI	-	-	0.4	-	-	0.4
Sodium sulfate	20.0	10.0	20.0	30.0	5.0	20.0
Mg sulfate	0.2	0.3	0.4	1.5	2.0	0.4
Protease	0.8	1.0	0.5	0.5	0.7	0.7
Amylase	0.5	0.4	-	0.25	0.4	0.2
Lipase	0.2	-	0.1	-	0.1	-
Cellulase	0.15	-	-	0.05	0.05	-

BNSDOCID: <WO 9913040A1 >

Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm	20ppm	10ppm
Perfume	0.3	0.3	0.1	0.2		
Brightener 1/2	0.05	0.2	0.08	0.1		
Misc/minors to 100%						

Example 7

The following compositions are pre-treatment compositions in accordance with the invention.

	AA	BB	CC	DD	EE	FF	GG	HH
LAS/AS	6.4	6.4	6.4	3.6	6.0	6.0	4.5	3.0
C23E3	8.6	-	-	-	-	-	1.5	-
C25E2.5S	-	4.0	9.0	12.0	6.0	6.0	1.5	3.0
ATC	-	3.5	3.5	3.5	3.5	3.5	-	-
H_2O_2	4.0	4.0	4.0	6.0	6.0	6.0	7.0	7.0
DTPA	0.2	0.4	-	1.0	0.4	0.8	1.0	0.5
HEDP	0.2	-	0.4	1.0	0.1	-	1.2	0.3
EDDS	0.2	0.2	0.4	-	0.1	0.8	0.2	-
NOBS	0.3	0.5	1.0	0.5	0.5	1.0	0.3	0.5
$MgSO_4$	1.3	0.1	0.2	0.2	0.3	0.8	1.5	0.5
Water and minors H2SO4 up to pH 4	---------- up to 100% ----------							

BNSDOCID: <WO 9913040A1 I >

WHAT IS CLAIMED IS:

1. A detergent composition comprising

(a) from 0.1% to 80% by weight of the composition of a bleaching system comprising a percarboxylic acid precursor of formula

$$R^1 - CO - L$$

wherein R^1 has at least 6 carbon atoms and L is a leaving group which is linked to the R^1 - CO- group with an oxygen atom.

(b) from 0.01% to 20% by weight of heavy metal ion sequestrants comprising at lease one

(i) phosphonate-containing heavy metal ion sequestrants; and at least one

(ii) carboxylate-containing heavy metal ion sequestrants;

(c) from 0.1% to 10% by weight of an alkali earth metal salt.

2. A detergent composition comprising

(a) from 0.1% to 80% by weight of the composition of a bleaching system comprising a percarboxylic acid of formula

$$R^1\text{-}CO_3M$$

wherein R^1 has at least 6 carbon atoms, and M is a counterion.

(b) from 0.01% to 20% by weight of heavy metal ion sequestrants comprising at least one

(i) phosphonate-containing heavy metal ion sequestrants; and at least one

(ii) carboxylate-containing heavy metal ion sequestrants;

(c) from 0.1% to 10% by weight of an alkali earth metal salt.

3. A detergent composition according to claim 1 or 2 wherein from 0.01% to 50% by weight of a phosphate-containing builder material is present.

4. A detergent composition according to any preceding claim which is a spray-dried particle -containing detergent composition.

5. A detergent composition according to any preceding claim wherein at least one heavy metal ion sequestrants has no oxidizable amino linkage and/ or one of the heavy metal ion sequestrants has an oxidizable amino linkage and a carboxylate group.

6 A detergent composition according to claim 1 wherein the bleaching system comprises a percarboxylic acid precursor, wherein L is an oxy benzene sulphonate and R^1 comprises 7 to 10 carbon atoms.

7. A detergent composition according to any preceding claim wherein the bleaching system comprises a hydrogen peroxide source, preferably comprising a percarbonate or perborate salt.

8. A detergent composition according to any preceding claim wherein at least one heavy metal sequestrant (i) is an amino alkylene poly (alkylene phosphonate), preferably selected from the group consisting of diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) and hexamethylene diamine tetra (methylene phosphonate).

9. A detergent composition according to any preceding claim wherein at least one heavy metal ion sequestrant (ii) is an ethylenediamine disuccinate, ethylene diamino acetic acid or nitriloacetic acid..

BNSDOCID: <WO 9913040A1 >

10. A detergent composition according to any preceding claim wherein at least one heavy metal ion sequestrant (i) is an organo diphosphonate preferably hydroxy-ethylene 1,1 diphosphonate.

11. A detergent composition according to any preceding claim wherein the alkali earth metal salt is a calcium or magnesium salt, preferably of sulphate, present at a level of from 0.2% to 5% by weight of the composition.

12. A detergent composition according to any preceding claim in the form of a solid composition, preferably a granular composition, preferably of bulk density of 330gr/litre to 600 gr/litre.

13. A method of washing laundry by hand whereby a solid detergent composition according to claim 12 is used.

14. A method of pre-treatment or soaking of laundry, whereby a detergent composition according to any of claims 1 to 12 is used.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/IB 98/01383

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/395 C11D3/36 C11D3/02 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 28531 A (PROCTER & GAMBLE ;BAILLELY GERARD MARCEL (GB); HARTSHORN RICHARD T) 19 September 1996 see example 3, composition D see claims 1-14 see page 13, line 4 - line 17 see page 43, line 16 - line 19	1,2,4,5, 7-11
X	WO 95 28463 A (PROCTER & GAMBLE ;MOSS MICHAEL ALAN JOHN (GB); SORRIE GRAHAM ALEXA) 26 October 1995 see example 3 see page 27, line 24 - page 28, line 18 see page 8, line 19 - page 9, line 18 see claims 1-23	1-3, 5-11,13, 14

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 January 1999	02/02/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Richards, M

1

Form PCT/ISA/210 (second sheet) (July 1992)

BNSDOCID: <WO 9913040A1 I >

INTERNATIONAL SEARCH REPORT

Inter ɔnal Application No
PCT/IB 98/01383

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 307 914 A (PROCTER & GAMBLE) 11 June 1997 see claims 1-14	1-10
A	EP 0 301 722 A (WARWICK INT LTD) 1 February 1989 see page 2, line 53 - page 3, line 33	1,2, 5-11,14
A	EP 0 778 342 A (PROCTER & GAMBLE) 11 June 1997 see example C see claims 1-15	1-10
P,A	EP 0 796 911 A (PROCTER & GAMBLE) 24 September 1997 see claims 1-6	/1,2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

BNSDOCID: <WO___9913040A1_I_>

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter onal Application No
PCT/IB 98/01383

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9628531 A	19-09-1996	AU 4984996 A	02-10-1996
		BR 9607217 A	07-07-1998
		CA 2214266 A	19-09-1996
		CZ 9702837 A	18-02-1998
		EP 0815192 A	07-01-1998
WO 9528463 A	26-10-1995	AU 2226995 A	10-11-1995
		BR 9507377 A	30-09-1997
		CA 2187307 A	26-10-1995
		CN 1150452 A	21-05-1997
		CZ 9602958 A	16-04-1997
		EP 0755430 A	29-01-1997
		HU 76033 A	30-06-1997
		JP 9512290 T	09-12-1997
GB 2307914 A	11-06-1997	CA 2238551 A	12-06-1997
		WO 9720907 A	12-06-1997
EP 0301722 A	01-02-1989	EP 0318470 A	31-05-1989
EP 0778342 A	11-06-1997	CA 2238577 A	12-06-1997
		WO 9720911 A	12-06-1997
EP 0796911 A	24-09-1997	WO 9735953 A	02-10-1997

RECEIVED
DEC 2 3 2002
INTELLECTUAL PROPERTY

BNSDOCID: <WO 9913040A1 I >